

Water Adsorption and Desorption by Coals and Chars

Esmail R. Monazam

*Department of Mechanical and Aerospace Engineering, West Virginia University,
Morgantown, West Virginia 26506*

Lawrence J. Shadle,* Renay Evans, and Karl Schroeder

*U.S. Department of Energy, Federal Energy Technology Center, P.O. Box 880
Morgantown, West Virginia 26507*

An investigation was carried out on the adsorption and desorption of moisture in chars of low-rank coal. Equilibrium moisture sorptions of dry and moist chars were measured at room temperature and at a relative humidity of 30% and 80%. On the basis of these measurements, a simple mathematical model was developed to predict both the rate and the level of hydration for coals and chars. The formulation uses a shrinking core model which required only the measurement of the adsorbing material's equilibrium moisture content at different temperatures and humidities. The model was validated against experimental and literature data. It accurately and reliably predicted both the rate and extent of hydration and dehydration for coals and char. Using this model, the effects of varying temperatures, relative humidities, and size of the particles and coal pile were simulated. The sensitivity study demonstrated that, as expected, relative humidity and temperature had strong effects on both the rate of hydration and the equilibrium moisture of coal or char. The particle size dramatically influenced the rate of hydration but had no effect on the equilibrium moisture content. This model can be used effectively to simulate the impact of moisture on drying, storage, and spontaneous combustion of coals and coal-derived chars.

Introduction

According to the U.S. Geological survey, a large proportion of the total fuel reserve in the United States is in high moisture, low-rank coal. These coals have been found to be expensive and difficult to transport. Drying and partial pyrolysis of coals minimizes these problems but raises another by increasing the susceptibility of the char to autoignition.^{1–4}

The Department of Energy has been actively engaged in a program toward understanding the spontaneous combustion of coal/char in storage. It has been reported in the literature^{1–4} that the presence of moisture in the form of high humidity is a major cause of autoignition. Therefore, a part of that program is devoted to developing a technique for predicting the rates of adsorption and desorption of moisture by stored char and coal. A study of moisture adsorption and desorption characteristics in both dry and moist coal and char was undertaken to provide a fundamental basis for such prediction.

Moisture has several potential effects on the self-heating of coals and chars. Foremost is the heat

released upon hydration of dried coals which can liberate sufficient heat to raise the coal temperature. Schmidt³ reported that the condensation of enough water to raise the moisture content of coal 1% is sufficient to raise its temperature 17 °C. This, in turn, increases the rate of oxidation more than 5-fold. Drying coals also dramatically effects the heat capacity of the coal such that reduced moisture content leads to a lower heat capacity.⁵ The effect is that dried low-rank coals have significantly increased tendencies to self-heat.

For low-rank coals, moisture also plays an integral role in the structure of the coal, which is considered to be "colloidal" or "gel-like" in nature.³ Upon drying and removal of "inherent" moisture, the gel structure is disrupted and shrinkage or "slacking" is observed.^{3,6} The Fleissner process⁷ uses steam to maintain an open structure during heating and drying to avoid such particle decrepitation. In addition, moisture interacts with oxygenated coal species and intermediates in the oxidation process. This interaction may alter the stability of the carbon–oxygen complexes and, thus, the rate of the weathering process.

Since all coal and char storage piles are exposed to air with some relative humidity, a quantitative knowledge of the rate of moisture adsorption and desorption

(1) Walker, I. K. *Fire Res. Abstr.* **1967**, 9, 5–22.

(2) Back, E. L. *Fire Saf. J.* **1981/1982**, 4, 185–196.

(3) Schmidt, L. D. In *Chemistry of Coal Utilization*; Lowry, H. H., Ed.; John Wiley & Sons Inc.: New York, 1945; Vol. 1, pp 627–676.

(4) Gauger A. W. In *Chemistry of Coal Utilization Vol. 1*; Lowry, H. H., Ed.; John Wiley & Sons Inc.: New York, 1945; Vol. 1, pp 600–626.

(5) Merrick, D. *Fuel* **1983**, 62, 540–546.

(6) Evans, D. G. *Fuel* **1973**, 52, 186–190.

(7) Oppelt, W. P.; Kube, W. R.; Kamps, T. W. *Bur. Mines. Rep. Invest.* **1959**, 5527.

is important. The present study describes a unique mathematical model that uses the relationships for equilibrium moisture content within a shrinking core model. This model predicts the rate of moisture adsorption and desorption by coal and/or char at various environmental conditions. The physical and chemical effects were directly incorporated into this model. The model presented here will describe the projected water sorption behavior in the absence of structural and mechanistic effects.

Experimental Section

A Piceance basin Wyodak coal was used to prepare char samples by heating coal (2 in. by 1/8 in. sieve size fraction) in a packed bed. The heating was done in two stages. In the first stage, the coal bed was heated by passing a hot flue gas stream through the bed to raise the temperature and remove moisture without initiating pyrolysis. In the second stage, a hot recycle gas stream from an external combustor was passed through the dried coal bed to further increase the temperature gradually up to 1000 °F before quenching. Dried char samples were taken from an indirectly cooled section and sealed in airtight steel cans, while moist char samples were removed downstream after passing through a rotating drum heat exchanger with direct water spray to introduce the desired amount of moisture. These were also sealed in airtight steel cans.

Rates of water adsorption and desorption for various coal and char samples were determined gravimetrically. A 10-g aliquot of each sample (mean diameter of 1 mm) was weighed into a Petri dish having a diameter of 82 mm. This provided a thin layer of sample only about 3 mm thick. The samples were placed in a constant humidity chamber consisting of a 10-L desiccator and a constant humidity solution. The rate of evaporation of the solution was increased by using paper towels as wicks around the circumference of the container. Different relative humidities (RH) were attained in the chamber using the following materials: anhydrous calcium sulfate (RH = 0%), saturated calcium chloride solution (30%), saturated calcium nitrate solution (50%), and saturated sodium chloride solution (80%).

The Petri dishes were removed from the chamber periodically, immediately covered with lids, weighed using a three-place analytical balance, and returned to the chamber. The rates were measured at room temperature.

At the conclusion of water sorption, the sample was dried in an oven at 110 °C with flowing nitrogen to determine the equilibrium moisture and initial moisture contents of the sample.

In a few experiments, the solution in the desiccator was agitated using a magnetic stirrer. The result of splashing of the solution and air current did not increase the rate of adsorption. This indicated that the rate of adsorption was not being limited by the rate of mass transfer of the moisture from the solution through the atmosphere to the coal.

Description of the Model. The modeling of the rate of sorption of moisture by a coal or char particles is a complicated process and involves consideration of physicochemical and physicochemical aspects of the moisture. Henderson¹⁰ applied Bangham's^{8,9} equations for the adsorption of vapor on coal/char to the equilibrium moisture content curves of a number of materials. He found the moisture content for the materials studied to have the following relationship with temperature (T) and relative humidity (RH)

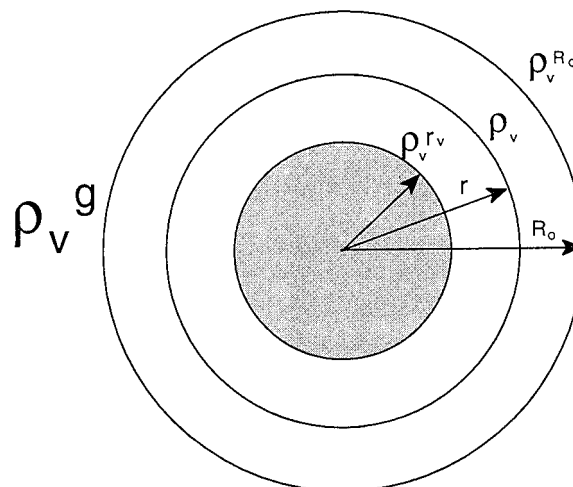


Figure 1. Schematic diagram of the shrinking core model showing the moisture vapor densities at different radii.

$$1 - RH = \exp(-KTM_e^n) \quad (1)$$

where M_e is the equilibrium moisture content of the solids represented on a dry basis. The factor K and exponent n vary for different materials.

It is well-known that there are three dominant types of water-coal linkage: chemically bonded water; water adsorbed by physicochemical forces; and free water held by physicochemical forces.^{4,13} Coal and char are considered to be hygroscopic materials¹² with micropores smaller than 1 μm in radius which fill with moisture with a weak bond energy (100 J/mol) to confining capillary walls. On the other hand, chemically attached moisture, such as water of crystallization, can have a bond energy of 5000 J/mol. The adsorption or desorption of lightly bound moisture will not change the material's form and properties significantly, but adsorption or desorption of strongly bound moisture will induce changes in the character of the solid. In this study, for modeling purposes, it is assumed that the rates of sorption of adsorbed and free water are dominant and may happen simultaneously. These rates are related to the gradient of vapor density between the saturation liquid at the evaporation/condensation surface and the gas phase. Bangham and Razouk⁹ described the adsorbed film formed by the vapor as a Langmuir monolayer in which the molecules have fixed points of attachment.

Therefore, applying the spherical geometry assumption portrayed in Figure 1, the rate of water sorption, \dot{r}_w , can be written as

$$\dot{r}_w = \frac{3r_v^2}{R_o^3} M_e \rho_p \frac{dr_v}{dt} \quad (2)$$

where r_v is the radius of the water sorption surface (Bangham's evaporation/condensation surface) at any time t . The rate of movement of the sorption surface can be obtained by a vapor balance at $r = r_v$

$$\frac{dr_v}{dt} = \frac{D_w}{M_e \rho_p} \frac{\partial \rho_v}{\partial r} \quad (3)$$

The moisture vapor profile within the particle in the region $r_v \leq r \leq R_o$ is provided by the solution of

(11) Evseev, V. S.; Voroshilov, S. P. *Sov. Min. Sci.* **1986**, 22, 140–146.

(12) Keey, R. B. *Drying Principles and Practice*; Pergamon: New York, 1972; Chapter 2.

(13) Arisoy, A.; Akgun, F. *Fuel* **1994**, 73, 281–286.

(8) Bangham, D. H. *Trans. Faraday Soc.* **1937**, 33, 805–811.

(9) Bangham, D. H.; Razouk, R. I. *Trans. Faraday Soc.* **1937**, 33, 1463–1472.

(10) Henderson, S. M. *Agricultural Eng.* **1952**, 1, 29–32.

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_w \frac{d\rho_v}{dr} \right) = 0 \quad (4)$$

with the boundary conditions at $r = R_0$

$$D_w \frac{d\rho_v}{dr} = K_g (\rho_v^R - \rho_v^S) \quad (5)$$

and at $r = r_v$

$$\rho_v = \rho_v^{r_v} \quad (6)$$

By combining eqs 3–6, the following equation can be derived

$$\frac{dr_v}{dt} = \frac{R_0^2 K_g (\rho_v^S - \rho_v^{r_v})}{M_e \rho_p r_v^2 \left(1 + BI_m \left(\frac{R_0}{r_v} - 1 \right) \right)} \quad (7)$$

where BI_m , K_g , D_w are the mass transfer Biot number, mass transfer coefficient (cm/s), and water diffusion coefficient (cm²/s) through the particle, respectively. The vapor radius is initially determined by the following equation

$$r_{v0} = R_0 \left(\frac{M_0}{M_e} \right)^{1/3} \quad (8)$$

where M_0 is the initial moisture and r_{v0} is the initial vapor radius. Arisoy and Akgun¹³ and McIntosh¹⁴ also used equations similar to eq 7 in their modeling efforts on the spontaneous combustion and drying process.

Finally, the differential equation for mass diffusion of moisture through the layer of a coal/char sample in the Petri dish of the experiment can be written as

$$\epsilon \frac{\partial \rho_v^S}{\partial t} = D_w^S \epsilon \frac{\partial^2 \rho_v^S}{\partial y^2} + (1 - \epsilon) r_w \quad (9)$$

where ϵ is the void fraction between the particles and y is the direction of moisture flow. The boundary conditions are

$$\rho_v^S = \rho_v^S \big|_{\text{surface}} \quad (10)$$

at $y = 0$ and

$$\frac{\partial \rho_v^S}{\partial y} = 0 \quad (11)$$

at $y = L$.

The moisture in the coal particle was calculated by

$$\rho_p \frac{\partial M}{\partial t} = r_w \quad (12)$$

where M is the coal moisture content (kg/kg).

Solution Procedure. The way in which moisture is adsorbed or desorbed by its host material and the knowledge of the moisture–solid equilibria is essential to the solution of these phenomena. Therefore, an attempt was made to measure the equilibrium moisture content of each sample as a function of relative humidity. However, to ease the experimental tasks, first the reliability of eq 1 was tested against the equilibrium moisture data of coal obtained by Glanville et al.¹⁵ and Nordon and Bainbridge.¹⁶ Their experimental data was limited to a temperature of approximately 25 °C. To obtain the values for K and n in eq 1, knowledge of the equilibrium moisture content as a function of the relative

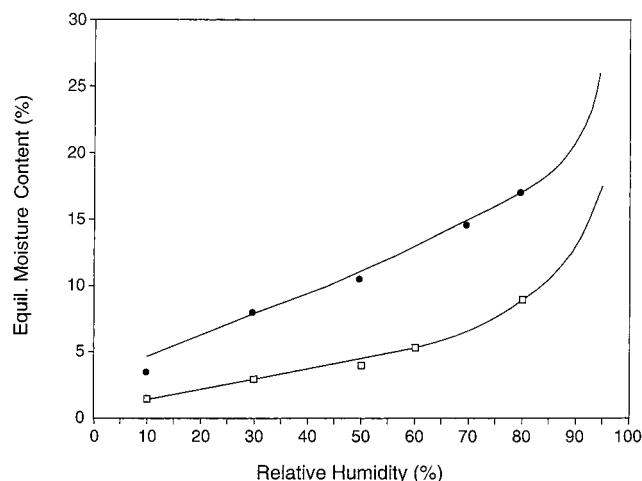


Figure 2. Comparison of the predicted (using eq 1 —) and experimental equilibrium moisture contents at 25 °C for different relative humidities. Data from (●) Glanville et al.,¹⁵ (□) Nordon and Bainbridge.¹⁶

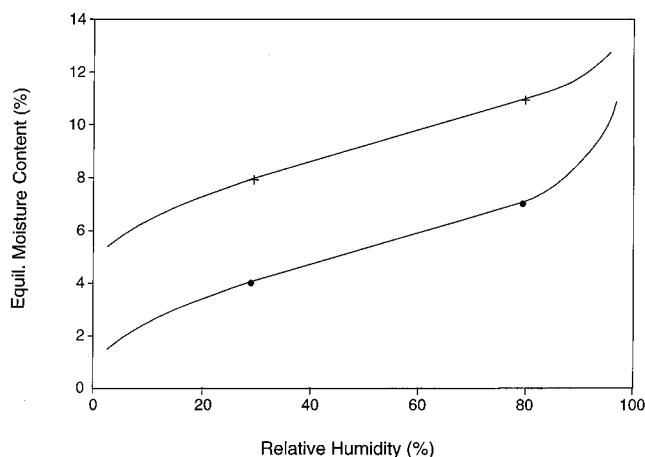


Figure 3. Solution of the equilibrium moisture equation (eq 1 —) for dry (●) and moist (+) Wyoming chars based on data at different relative humidities (30% and 80%) at 25 °C.

humidity is necessary. The nature of the correlation for eq 1 is shown in Figure 2 for two different chars from measured equilibrium moisture contents at two relative humidities.

In Figure 3 the equilibrium moisture content is presented for two Wyoming chars based on two measured points (equilibrium moisture content at 80% and 30% RH). The chars differed in their exposure to oxygen as well as their moisture contents. The moist char was partially oxidized for a short time at low temperatures. If a dry solid is exposed to an atmosphere of fixed relative humidity, it will gain moisture until equilibrium is reached. Increasing the relative humidity of the surroundings will then cause the solid to gain more moisture to reach another equilibrium state.

The water vapor at the core was assumed to be in equilibrium with the particle moisture content at all times, with its value as

$$\rho_v^{r_v} = RH_{r_v} \rho_s \quad (13)$$

where RH_{r_v} is the relative humidity at r_v , which is at equilibrium with the particle volume-averaged moisture content at any time t , M , and ρ_s is the saturation density at the particle temperature. The relative humidity (RH_{r_v}) is related to M according to eq 1 using the predetermined K and n for that sample from the equilibrium moisture measurements.

Equation 7 was solved using a fourth-order Runge–Kutta method. Since eq 7 is nonlinear, a small time step was

(14) McIntosh, M. J. *Fuel* **1976**, *55*, 47–52.

(15) Glanville, J. O., et al. *Fuel* **1986**, *65*, 647–649.

(16) Nordon, P.; Bainbridge, N. W. *Fuel* **1983**, *62*, 619–621.

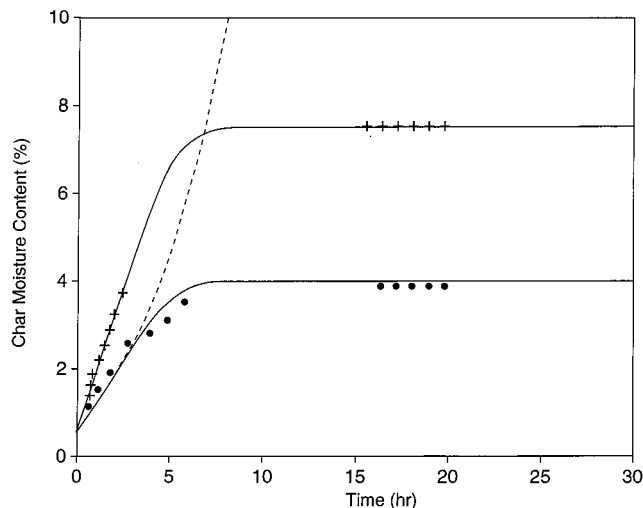


Figure 4. Single-particle model prediction (—) of the rate of hydration for a dry Wyoming char at 25 °C, $R_0 = 3$ mm, and different relative humidities: experimental data taken at 30% (●) and 80% (+). Model of Evseev and Voroshilov¹¹ for RH = 80% (---).

necessary for successful solution. This small time step allowed the use of r_v and M on the right-hand side of eq 7 at the previous time step. Use of an iteration technique did not improve the solution accuracy and increased the CPU time.

Equation 9 was transformed into the appropriate difference form for solution using an implicit Crank–Nicholson scheme and was solved numerically using Thomas' algorithm method.

Results and Discussion

The value of the vapor density ($\rho_v^{r_v}$) at the vapor core, eq 7, is the major factor in determining the movement of water vapor within the particle. The authors are aware of only one approach to estimate the $\rho_v^{r_v}$. In a study of spontaneous coal combustion, Evseev and Voroshilov¹¹ suggested that the vapor density on the sorption surface depends on the temperature and the energy of the water–coal bonding

$$\rho_v^{r_v} = \rho_s e^{-Q/RT} \quad (14)$$

where Q is the difference between the heat of evaporating water from the coal and that of free water. Q is equal to 2125 J/mol on average.¹¹ The approach of Evseev and Voroshilov was tested (Figure 4); however, the prediction resulted in high levels of water adsorption, unbounded by the coal's ability to adsorb moisture.

In this study, the sorption surface was defined based on the thermodynamic relationship between the equilibrium moisture content and the relative humidity as applied to agricultural materials.¹⁰ Therefore, an attempt was made to measure the equilibrium moisture content at different relative humidities for each sample under study. On the basis of these measurements, a relationship between the equilibrium moisture content and RH was obtained (eq 1). This approach included the dependence of the sorption surface on temperature, an effective water–coal bonding, and the equilibrium water capacity.

For the initial analysis of the hydration rate tests, the 3-mm thick layer was assumed to be a single particle with a radius of 3 mm and the rate of adsorption or

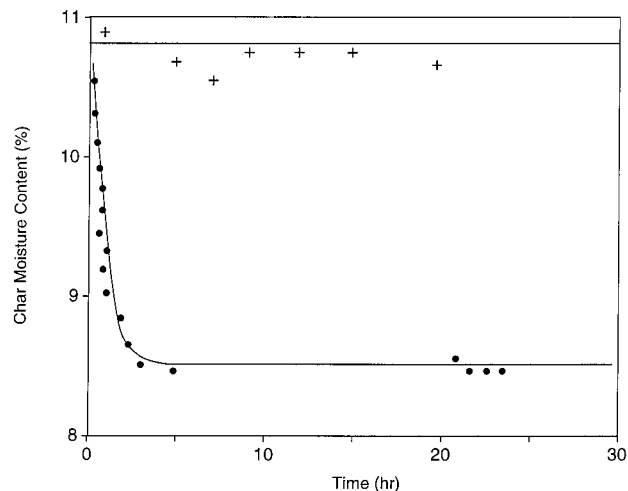


Figure 5. Single-particle model prediction (—) of the rate of hydration for a moist Wyoming char at 25 °C, $R_0 = 3$ mm, and different relative humidities: experimental data taken at 30% (●) and 80% (+).

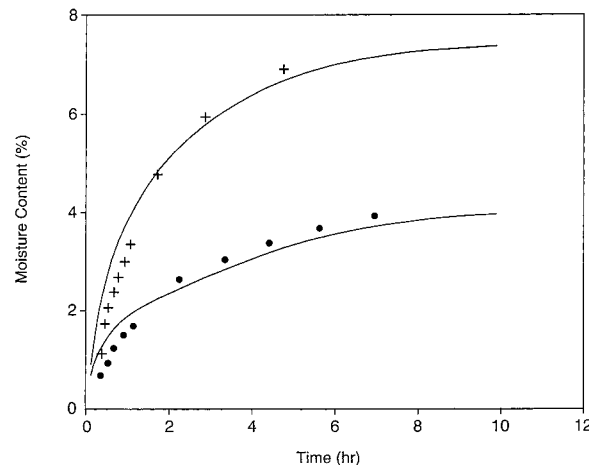


Figure 6. Fixed-bed model prediction (—) of the rate of hydration for a dry Wyoming char at 25 °C, $R_0 = 0.5$ mm, $L = 3$ mm, and different relative humidities: experimental data taken at 30% (●) and 80% (+).

desorption was predicted. The rate of water vapor movement within the single particle was obtained (eq 7) using a value of $0.0225 \text{ cm}^2/\text{s}$ ¹³ for the water diffusion (D_w) through the coal or char particle. The comparison between the model (as a single particle) and the experimental measurements is displayed in Figures 4 and 5. Good agreement was obtained for each sample studied. The slight fluctuations observed in the moisture content at the beginning of the rate measurement for Wyodak coal cannot be regarded as having any more significance than experimental errors.

The hydration tests were then analyzed considering the experimental Petri dish as a fixed bed with 3-mm thickness, a particle size of 1 mm in diameter, and zero gas velocity through the bed. Using combinations of eqs 7, 2, 9, and 12, the rate of adsorption or desorption was predicted and compared with the experimental data. The comparison of model prediction and test data demonstrated good agreement if the value of the diffusion coefficient of water through the bed (D_w^g) was the same as the diffusion coefficient of water through the particle ($0.0225 \text{ cm}^2/\text{s}$) (Figures 6 and 7). These simulations were performed assuming a void fraction of 0.35.

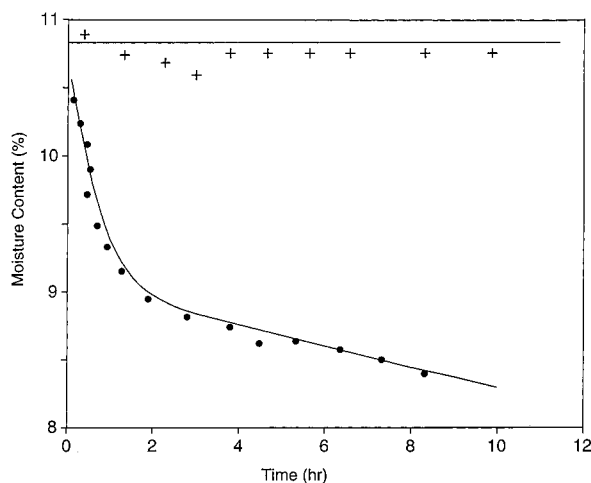


Figure 7. Fixed-bed model prediction (—) of the rate of hydration for a moist Wyoming char at 25 °C, $R_o = 0.5$ mm, $L = 3$ mm, and different relative humidities: experimental data taken at 30% (●) and 80% (+).

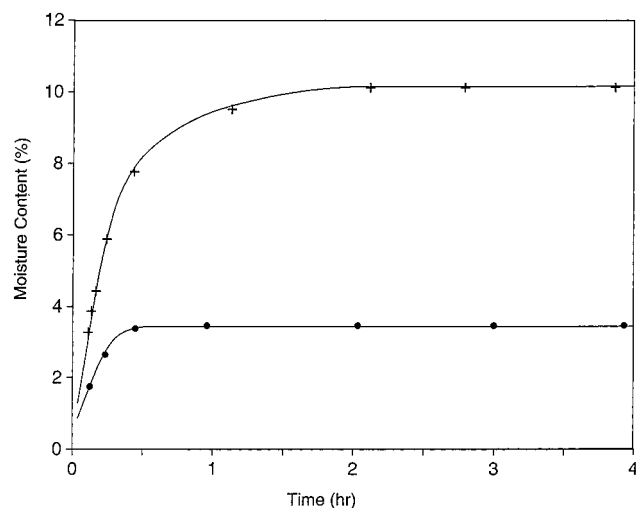


Figure 8. Fixed-bed model prediction (—) of the rate of hydration for a dry Yallourn-Briquette char from Nordorn et al.¹⁷ at 25 °C, $R_o = 0.5$ mm, $L = 3$ mm, and different relative humidities: experimental data taken at 38% (●) and 74% (+).

However, literature¹³ suggests that the dispersion coefficient of water through air ($D_{w,g}$) is about $0.25 \text{ cm}^2/\text{s}$. This dispersion coefficient is about 11 times greater than the value required by the model to match the test data. On the other hand, Nordon and Bainbridge¹⁷ measured the diffusion coefficient of water through the bulk char of 60% voidage to be 6.1 times less than coefficient of water through the air. Therefore, the value used in this study using 30% voidage is consistent with the Nordon and Bainbridge¹⁷ measured value and can be interpreted to represent the diffusion coefficient of water through the void spaces (air) within the char bed.

The model was also used to predict the rate of adsorption of water vapor by Yallourn-Briquette char published by Nordon and Bainbridge.¹⁷ A comparison between the model and experimental data was found to be in very good agreement, as displayed in Figure 8.

Sensitivity Study. To test further the utility of the model, the sensitivity of the rate of hydration was

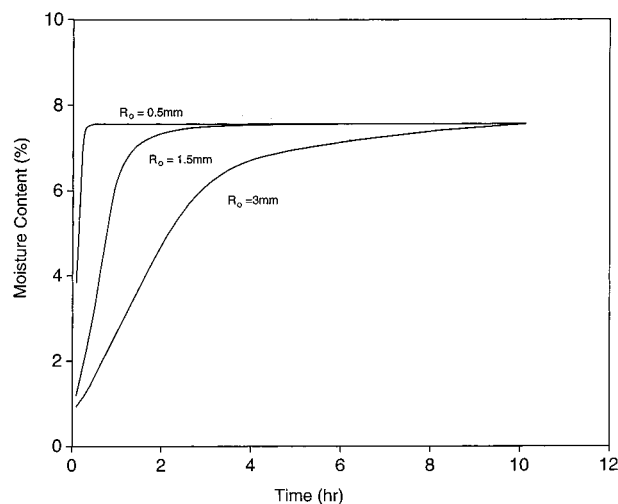


Figure 9. Sensitivity test of the single-particle model for rates of hydration using different particle sizes: $R_o = 0.5$, 1.5, and 3 mm.

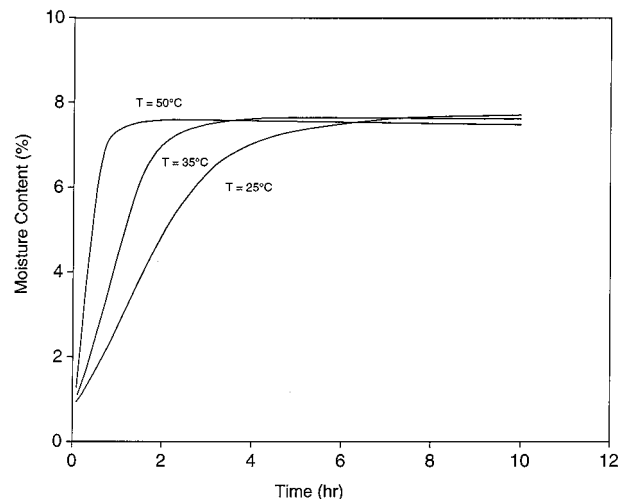


Figure 10. Sensitivity test of the single-particle model for equilibrium moisture content as a function of relative humidity for different temperatures $T = 25$, 35, and 50 °C.

examined for its response to some key physical parameters in the model. Parameter sensitivities were chosen to include the effect of particle size, temperature, and relative humidity on the rate of hydration for dry Wyoming char. For the sensitivity analysis, a baseline condition was selected. The base conditions included a particle size of 6 mm, temperature of 25 °C, and relative humidity of 80%. The rate of hydration for each of the model input parameters of interest was then examined by holding others constant while varying the value of the parameter under study.

The effect of changing the particle diameter on the resulting rate of hydration is illustrated in Figure 9. These prediction illustrated that the rate of hydration was a strong function of the diameter. The observed functional dependence arose from the fact that the rate of hydration is inversely proportional to diameter (eq 2).

The dependence of the rate of hydration on temperature is illustrated in Figure 10. These results show that the rate of hydration increased and the equilibrium moisture content decreased at a given relative humidity as the temperature increased. A strong dependence of

(17) Nordon, P.; Bainbridge, N. W. *Fuel* **1979**, *58*, 450–456.

the temperature on the rate of hydration is understandable because the rate (eq 7) is proportional to the core's equilibrium relative humidity. Upon inspection of eq 1, it is also clear that with increasing temperature, the relative humidity increases and the equilibrium moisture content at a given relative humidity decreases.

Variation of the relative humidity had a significant impact on the rate of hydration. This point is illustrated in Figure 5. These results are a direct consequence of eq 2, which indicate that the rate of hydration is proportional to the relative humidity.

Conclusion

A mathematical model has been presented for predicting the rate of adsorption or desorption of water vapor by char or coal particles. The model is based on the measured equilibrium moisture content for a specific coal or char at two different relative humidities. Excellent agreement between the model predictions and measurements on the rate of adsorption and/or desorption demonstrated that the model was accurate and reliable for calculating the rates of both hydration and drying.

The model was validated against experimental and literature data. It was found that the diffusion coefficient for water through a coal pile was the same order of magnitude as the diffusion of water within the particle.

To evaluate the effect of moisture on the self-heating of coal and chars in storage, knowledge of both the rate and amount of moisture sorption are necessary. The model presented here provides an accurate predictive tool for these quantities. With this capability, the rate of water sorption can be coupled with the heat of immersion to evaluate the effects of moisture on self-heating in coals and chars. This effect will be examined in the future.

A sensitivity analysis was performed on the rate of hydration. This rate depended on three essential parameters: the particle size, temperature, and relative humidity. As expected, the particle size strongly affected the rate of hydration, such that the rate was greater for smaller particles but had no impact on the equilibrium moisture content. The relative humidity strongly affected both the equilibrium moisture content

and the rate of hydration. Higher humidity resulted in a faster rate and higher moisture content. The temperature had a strong impact on the rate but only a slight effect on the equilibrium moisture content of the coal or char. As temperature was increased, the rate of hydration increased but the equilibrium moisture content decreased slightly.

Acknowledgment. The authors acknowledge the Department of Energy for funding the research through the Fossil Energy's Integrated Gasification Combined-Cycle program. Also, the authors acknowledge the reviews by Abolghasem Shamsi, Edward J. Boyle, Daniel Maloney, and Goodarz Ahmadi to provide a stronger manuscript.

Glossary

BI_m	mass transfer Biot number ($K_g d_p / D_w = 2$)
d_p	particle diameter (cm)
D_w^g	diffusivity of water into the gas within the char bed ($\text{cm}^2 \text{s}^{-1}$)
D_w	diffusivity of water into the particle ($\text{cm}^2 \text{s}^{-1}$)
K_g	mass transfer coefficient (cm s^{-1})
L	bed length (cm)
M	moisture content (kg kg^{-1})
M_e	equilibrium moisture content (kg kg^{-1})
M_0	initial moisture content (kg kg^{-1})
P	pressure ($\text{g cm}^{-1} \text{s}^{-2}$)
P_s	saturation pressure ($\text{g cm}^{-1} \text{s}^{-2}$)
r_v	vapor radius within the particle (cm)
r_w	rate of adsorption/desorption of moisture ($\text{g cm}^{-3} \text{s}^{-1}$)
R_0	particle radius (cm)
R	universal gas constant
RH	relative humidity
t	time (s)
T	temperature (K)
y	distance in the Y-direction (cm)

Greek Symbols

ϵ	bed voidage
ρ_p	particle density (g cm^{-3})
ρ_s	saturation density (g cm^{-3})
ρ_v	vapor density (g cm^{-3})
ρ_v^g	vapor density in the gas phase (g cm^{-3})
$\rho_v^{r_v}$	vapor density at the vapor radius (g cm^{-3})
ρ_v^R	vapor density at the particle surface (g cm^{-3})